

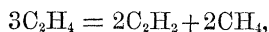
primary or secondary solution planes, hydration of the aluminium oxide takes place, and diaspora is formed, as shown by Lawrence Smith and Genth, and this unstable mineral enters into combination with silica and other oxides present to give rise to the numerous pseudomorphs of corundum, which are so well known to mineralogists.

There are certain crystals of corundum and spinel from Burma, which present illustrations of corrosion of a very remarkable and interesting character. Commencing with the formation of naturally etched figures ("Verwitterungsfiguren") the work of corrosion goes on till the whole crystal is broken up into an aggregate of simple forms—these being, in the case of the spinel, the octahedron, and in the case of the corundum, a combination of the rhombohedron, basal plane, and prism.

It is interesting to note that the quartz, feldspars, and other minerals associated with the rubies and spinels of Burma, exhibit phenomena of external etching and internal chemical change similar to those we have been describing in the case of the gems. The study of the whole of the phenomena throws much new light on the remarkable changes which take place, at great depth in the earth's crust, in minerals which, at the surface, appear to be of a very stable character.

II. "The Action of Heat upon Ethylene. II." By VIVIAN B. LEWES, Professor of Chemistry at the Royal Naval College, Greenwich. Communicated by Professor T. E. THORPE, F.R.S. Received January 10, 1895.

In a paper communicated to this Society in the spring of 1894,\* I showed that ethylene, when subjected to heat, was converted into acetylene and methane, according to the equation



and that the acetylene so formed either at once polymerised, forming a large number of secondary products, or else decomposed to carbon and hydrogen, according to the temperature at which the action was being carried on.

The fact that ethylene is one of the principal products in many cases of destructive distillation, renders a knowledge of the conditions affecting these changes of considerable importance, and the experiments described in this paper were made with the view of ascertaining the effect of rate of flow, area of heated surface, and dilution upon the changes taking place.

\* 'Roy. Soc. Proc.,' vol. 55, p. 90.

The apparatus and methods of analysis employed were the same as described in the former paper, with the exception that a platinum tube, 14 mm. in diameter and 73·6 cm. long, was used as the decomposing chamber, and that an easily regulated gas combustion furnace was employed as the source of heat. The temperature of the gas in the tube was measured as before, by the Le Chatelier thermo-couple, and every precaution was taken to keep it constant during the experiments.

The ethylene in each case was prepared by heating a mixture of 25 parts, by weight, of alcohol and 150 of strong sulphuric acid, purifying, and storing in a large glass holder.

The first set of experiments was to ascertain the influence of area of heated surface upon ethylene when passing through a tube heated to the temperature most often employed in the destructive distillation of coal and hydrocarbon oils, and also to find the result of varying the rate at which the gas was passed through the zone of heat.

Table I.—Influence of Rate of Flow and Length of Heated Surface upon the Amount of Ethylene decomposed. Temperature, 900° C. Rate of Flow, 5 c.c. per minute.

Length of tube heated .....	1 inch.	6 inches.	18 inches.
Volume of gas—before heating ..	525	625	625
"    "    after    "    "	490	653	670
Analysis of gaseous products.			
Carbon dioxide .....	0·75	0·50	0·75
Oxygen .....	0·50	0·25	1·00
Unsaturated hydrocarbons .....	17·80	10·75	2·75
Carbon monoxide .....	2·21	1·75	1·75
Saturated hydrocarbons by absorp.	11·25	9·50	12·22
"    "    by explos.	35·62	51·25	53·20
Hydrogen .....	24·12	22·75	24·00
Nitrogen .....	7·75	3·25	4·33

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated .....	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons .....	16·60	11·25	2·94
Saturated hydrocarbons .....	43·72	63·42	70·13
Hydrogen .....	22·50	23·75	25·72

The original gas, however, only contained 96·7 per cent. of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are:—

Length of tube heated .....	1 inch.	6 inches.	18 inches.
	80·1	85·48	93·76

Table II.—Temperature, 900° C. Rate of Flow, 15 c.c.

Length of tube heated .....	1 inch.	6 inches.	18 inches.
Volume of gas—before heating..	683	600	600
"    "    after    "    --	615	515	640
Analysis of gaseous products.			
Carbon dioxide .....	0·20	1·00	0·50
Oxygen .....	0·50	0·50	0·75
Unsaturated hydrocarbons .....	28·75	20·15	6·00
Carbon monoxide .....	1·50	1·50	1·75
Saturated hydrocarbons by absorp.	8·80	9·43	19·22
"    "    by explos.	33·45	42·37	37·50
Hydrogen ....	21·15	20·55	28·75
Nitrogen .....	5·65	4·50	5·53

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated .....	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons .....	25·87	17·28	6·39
Saturated hydrocarbons .....	38·02	44·44	60·46
Hydrogen .....	19·03	17·63	30·64

The original gas contained 96·7 per cent. of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are—

Length of tube heated .....	1 inch.	6 inches.	18 inches.
	70·83	79·42	90·31

Table III.—Temperature, 900° C. Rate of Flow, 40 c.c.

Length of tube heated .....	1 inch.	6 inches.	18 inches.
Volume of gas—before heating ..	870	1050	1000
„ „ after „ ..	790	985	980
Analysis of gaseous products.			
Carbon dioxide .....	0·75	0·50	0·25
Oxygen .....	0·50	0·75	0·50
Unsaturated hydrocarbons .....	50·80	35·75	9·75
Carbon monoxide .....	1·50	1·00	1·50
Saturated hydrocarbons by absorp.	11·22	11·25	10·00
„ „ by explos.	16·45	30·50	46·50
Hydrogen .....	14·50	16·65	28·00
Nitrogen .....	4·28	3·60	4·00

Calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.....	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons.....	46·12	33·53	9·55
Saturated hydrocarbons .....	25·12	39·16	55·37
Hydrogen .....	13·16	15·61	27·44

The original gas contained 96·7 per cent. of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are—

Length of tube heated .....	1 inch.	6 inches.	18 inches.
	50·58	63·17	87·15

On collecting these results in one table—

Percentage of ethylene decomposed.			
Length of tube heated .....	1 inch.	6 inches.	18 inches.
5 c.c. ....	80·10	85·48	93·76
15 c.c. ....	70·83	79·42	90·31
40 c.c. ....	50·58	63·17	87·15

The first thing that strikes one is the enormous amount of decomposition which takes place in the first inch of flow through the heated tube, and the small effect which an increase in the length of the heated surface has upon the further decomposition of the unsaturated hydrocarbons.

This result might be caused by the methane and hydrogen formed during the decomposition diluting the remaining ethylene, and so rendering the decomposition more difficult; it may also arise from secondary actions taking place amongst the primary products, and again forming ethylene, or it may be due to both these causes acting together.

In order to trace the effect of dilution, a series of experiments was made in which ethylene, diluted with hydrogen, was passed through 6 inches of the same tube as was used in the previous experiments, heated to the same temperature, and under precisely similar conditions.

The store holder of ethylene used for making the mixture contained a gas which gave, on analysis,

Ethylene .....	97·85
Nitrogen .....	2·00
Oxygen .....	0·15

Table IV.—Influence of Dilution in Checking Decomposition of Ethylene. Length of tube heated, 6 inches. Rate of Flow, 10 c.c. per minute. Temperature, 900° C.

Percentage of hydrogen .....	nil	10·0	25
„ ethylene .....	98·7	90·0	75
Volume of gas—before heating ..	100·0	100·0	100
„ „ after „ ..	81·3	69·5	69
Analysis of products of decomposition.			
Carbon dioxide .....	1·00	0·75	0·50
Oxygen .....	0·50	0·25	0·25
*Unsaturated hydrocarbons .....	32·52	31·00	29·00
Carbon monoxide .....	1·00	1·25	1·00
Saturated hydrocarbons by absorp.	17·75	14·50	14·50
„ „ by explos.	32·50	36·25	33·95
Hydrogen .....	12·62	14·25	18·50
Nitrogen .....	2·11	1·75	2·30
*Containing acetylene .....	1·06	0·52	0·73

Percentage of hydrogen .....	50	75	95
" ethylene .....	50	25	5
Volume of gas—before heating ..	100	100	100
" " after " "	64	85	100
Analysis of products of decomposition.			
Carbon dioxide .....	1.25	0.50	—
Oxygen .....	—	0.15	—
*Unsaturated hydrocarbons .....	22.25	11.10	2.00
Carbon monoxide .....	1.25	1.00	0.50
Saturated hydrocarbons by absorp.	8.50	5.50	0.75
" " by explos.	27.50	10.30	4.10
Hydrogen .....	37.15	68.45	89.15
Nitrogen .....	2.10	3.00	3.50
*Containing acetylene.....	0.32	0.15	trace

On calculating these percentages for the change in volume, we obtain the following results:—

	I.	II.	III.	IV.	V.	VI.
Unsaturated hydrocarbons ..	25.58	21.18	19.50	14.04	9.30	2.00
Saturated hydrocarbons ....	40.85	35.27	33.43	23.04	13.43	4.85

The ethylene taken only contained 97.85 per cent. of the hydrocarbon, hence—

	I.	II.	III.	IV.	V.	VI.
Unsaturated hydrocarbons originally present .....	97.85	88.02	73.35	48.90	24.45	4.89
Unsaturated hydrocarbons present after heating ....	25.58	21.18	19.50	14.04	9.30	2.00
Unsaturated hydrocarbons decomposed .....	72.27	66.84	53.85	34.88	15.15	2.89

and calculating this to percentage of total ethylene decomposed—

I.	II.	III.	IV.	V.	VI.
73.86	75.94	73.24	71.30	61.96	59.10

which shows that dilution has practically no effect in retarding the decomposition until 75 per cent. of diluent is present, and also clearly

points to its being radiant heat, and not contact with the heated sides of the tube, which is responsible for the largest proportion of the decomposition; since, had contact been the active factor, dilution, by reducing the number of impacts of the hydrocarbon molecules with the heated surface, would have shown a considerable decrease in decomposition.

Some information can be obtained as to the secondary reactions which accompany the main decomposition, by studying the proportions in which the products, other than ethylene, are present in the gases after heating.

Taking the experiments made upon the effect of length of heated tube and rate of flow, and tabulating the percentages of saturated hydrocarbons and hydrogen corrected for change of volume, we obtain the following results:—

#### Saturated Hydrocarbons.

Length of tube heated .....	1 inch.	6 inches.	18 inches.
5 c.c. ....	43·72	63·42	70·13
15 c.c. ....	38·02	44·44	60·46
40 c.c. ....	25·12	39·16	55·37

The temperature employed in these experiments is not sufficiently high to cause any large amount of the methane to decompose, so that the volume should, according to theory, approximate to two-thirds of the ethylene decomposed.

1 inch of heated tube.				
Rate of flow per minute.	Ethylene decomposed.	Methane found.	Calculated.	Variation.
5 c.c.	80·10	43·72	53·40	—9·68
15 c.c.	70·83	38·02	47·22	—9·20
40 c.c.	50·58	25·12	33·72	—8·60
6 inches of heated tube.				
5 c.c.	85·48	63·42	56·98	+6·44
15 c.c.	79·42	44·44	52·94	—8·50
40 c.c.	63·17	39·16	42·12	+2·96
18 inches of heated tube.				
5 c.c.	93·76	70·13	64·50	+5·63
15 c.c.	90·31	60·46	60·20	+0·26
40 c.c.	87·15	55·37	58·10	—2·73

The fact that when only 1 in. of tube is heated, there is a fairly constant deficit of the kind to be expected at the temperature employed, and that when a greater length of heated tube is used with a 5 c.c. rate of flow, the deficit becomes a substantial surplus, at once suggests that methane is amongst the secondary as well as the primary products of decomposition.

In the dilution experiments, the larger contraction in the volume noticeable points to the diluting of the products favouring polymerisation.

Dilution.	Ethylene decomposed.	Methane.		Variation.
		Found.	Calculated.	
Nil .....	72·27	40·85	48·18	-7·33
10 per cent. ..	66·84	35·27	44·56	-9·29
25    "    ..	53·85	33·43	35·90	-2·47
50    "    ..	34·88	23·04	23·24	-0·20
75    "    ..	15·15	13·43	10·10	+3·33
95    "    ..	2·89	4·85	1·92	+2·93

It seems probable from the figures that when dilution reaches above 50 per cent., not only is decomposition of the methane retarded, but formation as a secondary product commences.

Ever since water gas has been in use it has been well known that it contained traces of methane and acetylene, under conditions which render it impossible for them to have been formed from hydrocarbons remaining in the incandescent fuel, and the probabilities are that they have been produced, the acetylene by direct combination of carbon and hydrogen, and the methane by its partial decomposition.

The formation of ethylene from nascent hydrogen and acetylene takes place at such temperatures as those employed, and the amount so formed and again broken up by the radiant heat is purely a function of mass; so that I conceive from these experiments, the ethylene at once to a great extent decomposes under the influence of sufficiently high radiant heat according to the equation:—



and that the acetylene partly decomposes, the nascent hydrogen again uniting with more acetylene to reproduce ethylene, whilst other portions of the acetylene polymerise to benzene and other more complex hydrocarbons, and that, if the flow of this mixture be continued through a heated chamber, the action continues, the amount of ethylene regenerated becoming less and less, until it ceases to exist as a product of the decomposition.



It is well known that hydrogen will diffuse through ignited platinum into a vacuous space or even into other gases, and although no change in volume was observed when a mixture of 95 per cent. hydrogen and 5 per cent. ethylene was passed through the tube heated to 900° C., it seemed advisable to make special experiments to ascertain if any loss of hydrogen from this cause did take place at the temperature employed.

The apparatus having been fitted up as before, 6 in. of the tube were heated to between 900° and 1000° C., and a carefully measured volume of pure hydrogen was made to pass through it three times at a slow rate of flow, with the result that, after being brought back to its original temperature and pressure, it measured 99·5 per cent. of the volume taken, showing that error from this cause is not likely to have taken place.

A new series of experiments was now undertaken to ascertain, if possible, how increase of contact with the heated walls of the containing vessel affected the amount and character of the decomposition taking place.

In order to do this, a small platinum tube 2·5 mm. in diameter and 45·72 cm. long was taken in place of the one used in the previous experiments, which was 14 mm. in diameter. The area of the big tube therefore, as compared with the area of the small tube, was as 1·54 to 0·049, and in order to obtain the relative amount of decomposition it is manifest that the rate of flow must be the same in both tubes.

If the rate of flow in the big tube be 40 c.c. per minute, then

$$\frac{2\cdot5^2 \times 40}{14^2} = 1\cdot27$$

will give the required rate for the small tube.

Table V.—Temperature, 900° C. Rate of Flow, 1·27 c.c. per minute.

Length of tube heated .....	1 inch.	6 inches.	12 inches.
Volume of gas—before heating..	100	100	100
„ „ after „ ..	80	91	97
Analysis of gaseous products.			
Carbon dioxide .....	1·00	0·75	0·75
Oxygen .....	0·25	0·00	0·25
*Unsaturated hydrocarbons .....	15·30	12·20	6·30
Carbon monoxide .....	0·75	1·00	1·00
Saturated hydrocarbons by absorp.	13·50	12·10	9·50
„ „ by explos.	37·00	48·20	45·00
Hydrogen .....	26·00	18·75	30·80
Nitrogen .....	6·20	7·00	6·40
*Containing acetylene .....	0·3	0·32	0·20

Correcting the unsaturated hydrocarbons for change in volume, we obtain undecomposed—

I.	II.	III.
12·00	10·81	5·92

The ethylene used contained 96·75 per cent. of unsaturated hydrocarbons, therefore the amount decomposed is—

I.	II.	III.
84·75	85·94	90·83

Turning now to the experiments made with the large tube and 40 c.c. a minute rate of flow, we find that the percentage of ethylene decomposed was—

I. 1 inch.	II. 6 inches.	III. 12 inches.
50·58	63·17	75·16 calcd.

an increase of decomposition with the small tube amounting to the following percentages :—

I.	II.	III.
33·93	22·48	15·48

showing that the maximum increase of 34 per cent. rapidly falls with increased length of flow, whilst the ratio of area of heated surface to the passing gas is  $43\cdot96/7\cdot85$ , or 5·6 times as great in the small tube as in the large, yet only gives an increase of one-third at most in the decomposition.

From the results of these experiments it may be stated that—

1. The initial decomposition of ethylene by heat is very rapid, and requires but a short flow through a heated containing vessel, such primary decomposition, however, being but slowly completed, owing to secondary reactions, which tend to re-form ethylene.
2. Dilution has but little effect in retarding the decomposition of ethylene, unless it be very large.
3. Increase in rate of flow diminishes the amount of decomposition when the heated area is small, but rapidly diminishes in effect as the length of flow through a heated area increases.
4. The decomposition of ethylene is chiefly caused by radiant heat, the effect of which is very great as compared with the decomposition due to contact with heated surfaces.

I desire to acknowledge the valuable aid given me by Mr. F. B. Grundy in this investigation.

### III. "On the Measurement of Pressures by the Crusher-Gauge."

By W. KELLNER and W. H. DEERING. Communicated by Dr. W. ANDERSON, F.R.S. Received January 21, 1895.

The object of the experiments, the results of which are given in this paper, was to compare the indication of pressure (produced by the firing in a closed vessel of a gunpowder) by the crusher-gauge with a simultaneous estimation of the same pressure by another and simple method. This latter consisted in ascertaining the weight which was equal to the maximum pressure of the gases of the fired cordite (the smokeless gunpowder used in these experiments) acting on a valve closing gas-tight an opening in the explosion-vessel of area small enough to allow of the use of weights of manageable amount, not so small a fraction of the unit of surface (1 sq. in.) as to have to use a very large multiplier. Within the explosion-vessel, on the top of which were the valve and weights, was placed the crusher-gauge, the firing of the charge of cordite giving the two indications of pressure. In the "weights" method, a series of short steps was taken, weights in excess of that required being placed on the valve, the cordite fired, and it being observed whether the gases of explosion were blown out of, or kept in, the vessel. The amount of compression of the copper-crusher was then measured, and the corresponding pressure ascertained from the existing tables. In the next experiment the weights were lightened, and so on, until the gas blew out of the vessel, the mean of the pressure at the blow-out point and of that in the last experiment in